Determination of aragonite trace element distribution coefficients from speleothem calcite-aragonite transitions

J.A. Wassenburg[a*], D. Scholz[a], K.P. Jochum[b], H. Cheng[c,d], J. Oster[e], A. Immenhauser[f], D.K. Richter[f], T. Häger[a], R.A. Jamieson[g], J.U.L. Baldini[g], D. Hoffmann[h,i], S.F.M. Breitenbach[j]

Affiliations:

[a]Institute for Geosciences, University of Mainz, Mainz, Germany
[b]Climate Geochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany
[c]Institute of Global Environmental Change, Xian Jiaotong University, Xian, China
[d]Department of Earth Sciences, University of Minnesota, Minneapolis, USA
[e]Department of Earth and Environmental Sciences, Vanderbilt University, Nashville, TN, USA
[f]Institute of Geology, Mineralogy and Geophysics, Ruhr-University Bochum, Bochum, Germany
[g]Department of Earth Sciences, Durham University, Durham, United Kingdom
[h]Max Planck Institute for Evolutionary Anthropology, Department of Human Evolution, Leipzig, Germany
[i]Bristol Isotope Group, School of Geographical Sciences, University of Bristol, Bristol, UK
[j]Department of Earth Sciences, University of Cambridge, Cambridge, UK

*Corresponding author

Email:	wassenbu@uni-mainz.de
Tel.:	+49 6131-39-23170
Fax:	+49 6131 39 23070
Address:	Johann-Joachim-Becher-Weg 21
	55128 Mainz, Germany

Abstract:

The processes that govern the incorporation of (trace) elements into speleothems can often be linked to environmental changes. Although element incorporation into speleothem *calcite* is now reasonably well understood, current knowledge regarding trace element variability in speleothem *aragonite* is very limited. Of particular interest is whether trace element distribution coefficients are above or below one in order to assess the extent to which prior aragonite precipitation has affected speleothem aragonite trace element records.

This study uses nine calcite-to-aragonite transitions in seven speleothems from diverse environmental settings to derive the first quantitative estimates of the distribution coefficients for several elements in speleothem *aragonite:* $D_{Mg(Ar)}$ = 9.7E-5 ± 9.01E-5, $D_{Ba(Ar)}$ = 0.91 ± 0.88, $D_{Sr(Ar)}$ = 1.38 ± 0.53, and $D_{U(Ar)}$ = 6.26 ± 4.54 (1σ SD). For one speleothem from western Germany, the distribution coefficients are generally higher, which is potentially related to the very low growth rates (<11 µm/year) of this sample. In particular, $D_{Sr(Ar)}$ appears to show a negative correlation with growth rate when growth rate is below 20 µm/year.

In summary, our results demonstrate that speleothem aragonite $D_{Mg(Ar)}$ is below one, $D_{U(Ar)}$ is considerably above one, and $D_{Sr(Ar)}$ is above one or close to unity. For $D_{Ba(Ar)}$, reaching a similar conclusion is difficult due to the relatively high uncertainty. Enhanced prior aragonite precipitation will thus result in lower U and higher Mg concentrations in speleothem aragonite, although in many cases Mg in speleothem aragonite is most likely dominated by other processes. This result suggests that U concentrations in aragonitic stalagmites could serve as very effective proxies for palaeo-rainfall.

1. Introduction

Speleothems are secondary cave deposits mainly consisting of calcite or aragonite with calcite being the more common polymorph of $CaCO_3$ (Hill and Forti, 1997). Speleothems, and in particular stalagmites and flowstones are considered as some of the most promising continental climate archives. They can serve as benchmarks, which can be reliably contrasted and compared with proxy records from complementary archives, because they can be precisely dated up to about 500 ka by the ^{230}Th/U-dating technique (e.g., Scholz and Hoffmann, 2008). In addition, speleothem archives can be sampled and analysed with up to sub-annual resolution for carbon and oxygen isotopes (Mattey et al., 2008; McDermott, 2004; Myers et al., 2015) and trace and major elemental abundances (Fairchild and Treble, 2009). Numerous studies on speleothem calcite trace element compositions have been published recently (Borsato et al., 2007; Day and Henderson, 2013; Fairchild and Treble, 2009; Griffiths et al., 2010; Treble et al., 2005; and references therein). Few studies, however, focus on trace element compositions in aragonite speleothems (Finch et al., 2003; Finch et al., 2001; McMillan et al., 2005; Tan et al., 2014; Wassenburg et al., 2012; Wassenburg et al., 2013). The knowledge on element partitioning into speleothem aragonite is thus very limited.

Since aragonite speleothems contain much more U compared to their calcitic counterparts, they can provide excellent age models (Cosford et al., 2008; Myers et al., 2015; Ridley et al., 2015). However, aragonite is metastable and may recrystallize to calcite under certain conditions, which results in post-depositional open system behaviour of the U-series system and apparently incorrect ^{230}Th/U-ages (Lachniet et al., 2012; Ortega et al., 2005). Where robust evidence that an aragonite speleothem is well preserved is available (Myers et al., 2015; Wassenburg et al., 2013), the potential to obtain exceptionally precise chronologies is high. Consequently, it is important to further investigate (i) how trace elements partition into speleothem aragonite and (ii) which controls and processes are reflected by their temporal and spatial variability.

The major crystallographic difference between calcite and aragonite lies in their different crystal structures. Aragonite is characterized by an orthorhombic crystallography, where the Ca-ion is coordinated by nine O-ions, whereas calcite has a trigonal crystallography, where the Ca-ion is coordinated by six O-ions (Swart, 2015). Due to these crystallographic differences, larger cations, such as Sr, Ba and U, are preferentially incorporated into aragonite, whereas calcite also tends to incorporate small cations, such as Mg. The corresponding trace element distribution coefficients, D_X, are defined as:

$$D_X = \frac{X/Ca_{Solid}}{X/Ca_{Solution}}, \quad (1)$$

where X represents a certain trace element. Due to the crystallographic differences, the distribution coefficients may be very different for calcite and aragonite.

Recently, Stoll et al. (2012) introduced a model that facilitates quantitative interpretations of speleothem calcite Mg, Ba, and Sr signals in terms of prior calcite precipitation (PCP) (Fairchild et al., 2000). This process refers to the precipitation of calcite before the dripwater reaches the stalagmite (Fairchild and Treble, 2009), which occurs when the dripwater encounters empty voids within the karst with a lower partial CO_2 pressure compared to the water. This forces degassing of CO_2, temporarily increasing supersaturation with respect to calcite and calcite precipitation. PCP usually refers to calcite precipitation in the aquifer above the cave, although it may also occur inside the cave (e.g., at the cave ceiling or on the surface of a stalactite). Certain environmental conditions may favour prior aragonite precipitation (PAP) instead of PCP. Fairchild and Treble (2009) first mentioned PAP, which was subsequently documented and detailed by Wassenburg et al. (2013). Both PCP and PAP are enhanced during periods of reduced aquifer recharge when more time is available for degassing and more air-filled voids exist in the aquifer. If trace element distribution coefficients are below (above) one, elevated concentrations in speleothems are typically interpreted as reflecting reduced (enhanced) infiltration and drier (wetter) climatic conditions (Johnson et al., 2006). However, cave ventilation may also control PCP (Sherwin and Baldini, 2011; Wong et al., 2011).

Quantitative and qualitative interpretations of speleothem trace element records strongly depend on well constrained D_X values. Laboratory precipitation experiments indicate that for calcite, temperature might affect $D_{Mg(Cc)}$ (Day and Henderson, 2013; Oomori et al., 1987). Other experiments suggest that precipitation rates (Gabitov et al., 2014; Lorens, 1981; Tesoriero and Pankow, 1996) and/or solution composition (Mucci and Morse, 1983; Pingitore and Eastman, 1986) may control $D_{Mg(Cc)}$, $D_{Sr(Cc)}$, and $D_{Ba(Cc)}$. For aragonite, temperature may affect trace element distribution coefficients for Mg, Ba, and Sr (Dietzel et al., 2004; Gaetani and Cohen, 2006), whereas precipitation rates may influence aragonite distribution coefficients for U and Mg (Gabitov et al., 2008).

However, most of these experiments were designed to reflect marine environments. Within cave environments, the conditions driving $CaCO_3$ precipitation are very different. Spelean $CaCO_3$ precipitation is driven by rapid degassing of CO_2 from thin water films

(Hansen et al., 2013) with low ionic strength and the presence of (organic) colloidal phases (Fairchild and Treble, 2009; Hartland et al., 2014), whereas marine deposition occurs in high ionic strength waters and is often biologically mediated. The same arguments prompted a series of studies that aimed to determine speleothem calcite D_X. These were based on both field precipitation experiments, during which the trace element composition of calcite farmed within a cave over a known time period is compared with the trace element composition of the associated dripwater (Fairchild et al., 2010; Gascoyne, 1983; Huang et al., 2001; Karmann et al., 2007; Riechelmann et al., 2014; Tremaine and Froelich, 2013), and cave analogue laboratory experiments (Day and Henderson, 2013; Huang and Fairchild, 2001). These experiments demonstrate that Dx values determined under karst analogue conditions are different from those in marine environments. Consequently, Dx values determined under marine conditions are not necessarily transferable to karst settings, and doing so may lead to incorrect climate interpretations.

Karst analogue experiments aiming to determine Dx values for aragonitic stalagmites have not been performed yet. Thus, these values remain almost entirely unknown. For speleothem aragonite, only one $D_{Sr(Ar)}$ estimate is available, which is based on modern dripwater Sr/Ca ratios corresponding to an actively growing stalagmite, the Sr concentration at the top of the calcitic stalagmite and the ratio of the Sr content of a calcite and an aragonite phase that precipitated approximately 900 years ago (McMillan et al., 2005). In order to advance the present understanding, we analyse published (McMillan et al., 2005; Wassenburg et al., 2012) and new trace element data from calcite-aragonite transitions in speleothems to derive speleothem aragonite $D_{X(Ar)}$ values for Mg, Sr, Ba and U. To our knowledge, this study provides the first aragonite $D_{X(Ar)}$ values determined entirely under cave environmental conditions.

2. Cave settings

The data presented here are derived from speleothems from different geographic and environmental settings (Fig. 1): Grotte Prison de Chien and Grotte de Piste (Morocco) (Wassenburg et al., 2012), Mawmluh Cave (Breitenbach et al., 2015) and Krem Umsynrang Cave (NE India), an unnamed cave located 8 km south of Trevélez (S Spain) (Richter et al., 2002), Grotte de Clamouse (S France) (Frisia et al., 2002; McMillan et al., 2005), and Hüttenbläserschachthöhle (Central Germany) (Jochum et al., 2012; Yang et al., 2015). We emphasize that the settings of these caves cover a wide range of climates varying from summer dry temperate, all year wet temperate, to summer wet temperate conditions (Peel et

al., 2007). For most of the caves, dolostone is a primary host rock component (Table 1). This results in high dripwater Mg/Ca ratios, one of the boundary conditions to precipitate aragonite (Riechelmann et al., 2014). For further details, the reader is referred to Table 1.

3. Materials and methods

3.1. Samples

For this study, both lateral and stratigraphic calcite-aragonite (Cc-Ar) transitions from seven speleothems were investigated (Table 1; Fig. 1 and 2). Datasets from Grotte de Clamouse (Frisia et al., 2002; McMillan et al., 2005) as well as Grotte Prison de Chien and Grotte de Piste (Wassenburg et al., 2012) were previously published, and the reader is referred to these publications for a detailed documentation of these samples. In addition, one Cc-Ar transition in each of the stalagmites KRUM11 (Krem Umsynrang Cave), MAW4 (Mawmluh Cave; Breitenbach et al., 2015), and MO (unnamed cave) were analysed. Furthermore, four transitions in stalagmite HBSH1 (Hüttenbläserschachthöhle; Jochum et al., 2012; Yang et al., 2015) were studied in detail.

Sample KRUM11 is approximately 280 mm long and consists of two parallel stalagmites, which lay on the cave floor when collected. On top of those, a younger, 52 mm long speleothem grew upwards, perpendicularly to the broken precursor sample. The sample exhibits a stratigraphic Cc-Ar transition in the older part of the speleothem and a lateral Cc-Ar transition in the youngest part (Fig. 2). Stalagmite MAW4 is 30 mm long and actively grew at the time of collection in March 2006. MAW4 contains one stratigraphic Cc-Ar transition (Fig. 2). Flowstone MO has a maximum thickness of 74 mm and exhibits multiple stratigraphic and lateral Cc-Ar transitions (Fig. 2). Stalagmite HBSH1 is described in Yang et al. (2015). For all samples, the boundaries between calcite and aragonite mineralogies are macroscopically visible and distinct (Fig. 2).

3.2. Petrography

Aragonite is a polymorph of $CaCO_3$ and metastable under Earth surface conditions. Thus, it has a tendency to recrystallize to calcite within months to up to hundred's of thousands of years when exposed to diagenetic fluids (Frisia et al., 2002; Lachniet et al., 2012; Martin-Garcia et al., 2009; Perrin et al., 2014; Zhang et al., 2014). In this study, thin-sections were examined under a polarization microscope in order to assess whether the samples show petrographic evidence for diagenetic alteration. Diagenetic alteration of calcite

and aragonite can be identified by the appearance of dissolution features (Figs. 9c and 10 in Perrin et al., 2014), micritization and aragonite relics (Figs. 3 and 8 in Martin-Garcia et al., 2009) and calcite mosaics (Fig. 14 in Frisia and Borsato, 2010, and Fig. 3 in Scholz et al., 2014). In addition, the mineralogy of the samples was determined by X-ray diffraction at the ETH Zurich, Switzerland, using approximately 30 mg of sample powder, as well as by Raman spectroscopy performed at the University of Mainz, Germany. The Raman spectrometer used was a HR 800 from the company Horiba Jobin Yvon, with an attached Olympus BX41 Microscope equipped with an automatic xyz-stage to undertake the 2-dimensional mappings. A frequency doubled Nd-YAG laser (532.12nm), a grating of 1800 grooves/mm, an entrance slit of 100 μm and a confocal hole of 400 μm were used for the measurements. Every point was measured twice to eliminate spikes; each measurement was performed with an accumulation time of 1 s. To evaluate the calcite content, the intensity of the band at 282 cm^{-1} was used. For aragonite, the band at ca. 207 cm^{-1} was used.

3.3. Dating

Dating of all samples was performed by the ^{230}Th/U-method to assess whether the speleothems grew continuously across the Cc-Ar transitions and to quantify growth rates. Four samples from stalagmite MAW4 were dated at the Minnesota Isotope Laboratory at the University of Minnesota, USA, with a multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS, Thermo Finnigan Neptune-Plus) following the procedures described by Cheng et al. (2000), Cheng et al. (2013), and Edwards et al. (1987). Two samples from stalagmite KRUM11 and four samples from flowstone MO were dated using a Nu Plasma MC-ICPMS at the Max Planck Institute for Chemistry, Mainz, Germany, following the procedures of Obert et al. (2016). The top sample of flowstone MO was dated at the Helmholtz Centre for Ocean Research Kiel (GEOMAR) following the procedure of Fietzke et al. (2005). Eight samples from stalagmite HBSH1 were dated at Bristol University, UK, following the procedures described by Hoffmann et al. (2007). All ages are reported as thousands of years before present (ka BP) with reference to the year 1950 AD.

3.4. Trace element analysis

Trace element compositions of sub-samples from speleothems KRUM-11, MAW-4, and MO were analysed at the Max Planck Institute for Chemistry, Mainz, Germany. Mg/Ca, Al/Ca, Si/Ca, P/Ca, Mn/Ca, Sr/Ca, Y/Ca, Ba/Ca, Pb/Ca, Th/Ca, and U/Ca ratios were determined with a Thermo Finnigan Element 2 Inductively Coupled Plasma Mass

Spectrometer (ICPMS) coupled to a New Wave UP213 laser ablation system. The isotopes ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{43}Ca, ^{55}Mn, ^{88}Sr, ^{89}Y, ^{137}Ba, ^{208}Pb, ^{232}Th, and ^{238}U were used. Pre-ablation was performed using an 80 µm spot size at a scan speed of 80 µm/s to clean the sample surface. The line scan technique was employed using a scan speed of 5 µm/s and a 55 µm spot size. Samples were ablated with a pulse rate of 10 Hz and an energy density of 9.5 J/cm2. Laser warm-up time (i.e., blank measurement time) was set at 11 s. In order to assess potential sample inhomogeneity, ten individual spot analyses were performed parallel to the line scans at a distance of approximately 100 µm using a 100 µm spot size, an energy density of 10.4 J/cm^2 and a total dwell time of 70 s, including an 11 s blank measurement. Both the line scans and the single spot transects covered the Cc-Ar transitions of interest. Measurements were corrected for background, and ^{43}Ca was used as an internal standard to convert count rates into trace element/Ca mass ratios, which were then converted into molar ratios in order to calculate distribution coefficients. Relative sensitivity factors were determined using the NIST612 glass and MACS3 $CaCO_3$ reference materials using the values published in Jochum et al. (2012). In order to avoid matrix effects, Pb was corrected using the relative sensitivity factor derived from MACS3 (Jochum et al., 2012). Three NIST612 and MACS3 analyses, respectively, were performed ca. every hour of sample analysis in order to assess and correct for a potential drift of the mass spectrometer. The line scan data were smoothed with a 5-point-running median. For further information on the methodology and data evaluation, the reader is referred to Jochum et al. (2009; 2012).

The Cc-Ar transitions from stalagmite HBSH1 were analysed at Bristol University, UK. Mg/Ca, P/Ca, Sr/Ca, Y/Ca, Ba/Ca, Pb/Ca, Th/Ca and U/Ca were determined with a NewWave UP193HE Excimer laser coupled to a Thermo Finnigan Element2 ICPMS. The isotopes ^{26}Mg, ^{31}P, ^{43}Ca, ^{88}Sr, ^{89}Y, ^{137}Ba, ^{208}Pb, ^{232}Th, and ^{238}U were used for analysis. Spots were ablated at 200 µm resolution with a 30 µm spot size. The laser warm-up time was set at 40 s (blank measurement time), followed by 104 s of ablation and 60 s wash-out. ^{43}Ca was used as an internal standard to convert count rates into concentrations. Samples were ablated with an energy density of 5 J/cm^2 and a pulse rate of 5 Hz. The glass reference materials NIST610 and NIST612 were used for calibration. Data evaluation was performed with the software package "Glitter".

The uncertainty of the trace element results is represented by the relative standard deviation associated with the mean trace element concentration of the reference materials NIST610 and NIST612 for speleothem HBSH1. For speleothems KRUM11, MAW4 and MO, uncertainties were determined by calculating a mean uncertainty from the individual MACS3

line scans. For speleothem HBSH1, only glass reference materials were measured. Since the trace element concentrations of these reference materials differ, it is possible to use a different uncertainty for high and low trace element concentrations. This is an advantage considering the difference in trace element concentrations between calcite and aragonite. For an overview, the reader is referred to Table 2. The uncertainties for trace element concentrations in speleothems HK3 and GP2 are based on the MACS1 reference material and were published by Wassenburg et al. (2012).

3.5. Derivation of speleothem aragonite distribution coefficients

3.5.1. Approach

Aragonite distribution coefficients were determined using the following procedure: Firstly, we calculated the trace element/Ca ratio of the dripwater feeding the stalagmite using the trace element/Ca ratio of the calcite section of the corresponding Cc-Ar transition and the calcite distribution coefficients (Day and Henderson, 2013). Assuming that the dripwater trace element/Ca ratio did not undergo major changes with time, the speleothem aragonite distribution coefficient can be estimated by combining the trace element/Ca ratio of the aragonite section of the transition and the calculated trace element/Ca ratio of the dripwater.

This approach can be mathematically summarized as follows: The distribution coefficient is a function of the trace element to Ca ratio of the solid divided by the trace element to Ca ratio of the solution (i.e. equation 1). Thus, the calcite distribution coefficient, $D_{X(Cc)}$, is given by:

$$D_{X(Cc)} = \frac{X/Ca_{Cc}}{X/Ca_{Solution}} \quad (2)$$

Accordingly, the distribution coefficient for aragonite $D_{X(Ar)}$ is given by:

$$D_{X(Ar)} = \frac{X/Ca_{Ar}}{X/Ca_{Solution}} \quad (3)$$

$D_{X(Cc)}$ is available from previous studies (Day and Henderson, 2013), and $X/Ca_{(Cc)}$ and $X/Ca_{(Ar)}$ are measured values. Using the assumption that the dripwater trace element/Ca ratio was similar for precipitation of calcite and aragonite (see below for a critical discussion),

289 $X/Ca_{Solution}$ can be calculated from equation (2). Inserting this value in Eq. (3), $D_{X(Ar)}$ can be
290 calculated. In summary, $D_{X(Ar)}$ is given by:
291
292 $$D_{X(Ar)} = \frac{X/Ca_{Ar}}{X/Ca_{Cc}/D_{X(Cc)}} \quad (4)$$

293
294 The calcite distribution coefficients used for the calculations were taken from the
295 cave-analogue precipitation experiments performed by Day and Henderson (2013). These are:
296 $D_{Mg(Cc)} = 0.01*e^{0.02*T}$, $D_{Sr(Cc)} = 0.12$ and $D_{Ba(Cc)} = 0.11$. According to the experiments from
297 Day and Henderson (2013), the relation between $D_{Sr(Cc)}$ and temperature was statistically not
298 significant, for $D_{Ba(Cc)}$ no relation could be identified either. Day and Henderson (2013)
299 indicate that $D_{U(Cc)}$ does not show a clear relationship with temperature although the D_U
300 values for experiments conducted at 7°C and 15°C were slightly different (i.e., 0.11 and 0.12,
301 respectively). Therefore, we estimated cave temperatures during speleothem growth from the
302 literature and cave monitoring data and used the corresponding values for $D_{U(Cc)}$ and $D_{Mg(Cc)}$.
303 Our approach strongly depends on the validity of the assumption that the trace
304 element/Ca ratio of the dripwater did not undergo a major change during the time covered by
305 the Cc-Ar transition. However, in order to initiate aragonite precipitation, a change in
306 dripwater chemistry is absolutely necessary (Frisia et al., 2002; Riechelmann et al., 2014;
307 Wassenburg et al., 2012). At first glance this seems to be contradictory to our assumption, but
308 if the potential change in dripwater chemistry is accounted for by the uncertainty assigned to
309 the values used for the calculations, the error introduced by our assumption can be propagated
310 to the calculated aragonite distribution coefficients. This is critically discussed in the next
311 section.

312
313 3.5.2. Error propagation
314 Because assessing potential past changes in dripwater trace element composition is
315 challenging, speleothem trace element data variability must be considered carefully. In order
316 to solve this, we included the standard deviation of the trace element data in the error
317 propagation of the aragonite distribution coefficients. In addition, the uncertainty of the trace
318 element analysis and the uncertainty related to the published calcite trace element distribution
319 coefficients (Day and Henderson, 2013) are included. The error bars on the calculated

aragonite distribution coefficients are, thus, very conservative. We used the following equation to calculate the absolute error of the speleothem aragonite D_X values:

$$\Delta D_{X(Ar)} = D_{X(Ar)} * \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2}, \quad (5)$$

where σ_1 is the relative standard deviation determined from the external reference materials (Table 2), σ_2 is the relative uncertainty of the calcite distribution coefficient (Day and Henderson, 2013), and σ_3 and σ_4 are the relative uncertainties of the mean calcite and aragonite trace element to Ca ratios. We note that a potential change in drip water composition during the time that the mineralogy changed from calcite to aragonite remains challenging to assess, therefore we cannot incorporate a fixed uncertainty in the error propagation. However, in the results and interpretation section we discuss the effect of an additional 50% uncertainty of the mean trace element values.

3.5.3. Boundary conditions for aragonite precipitation

For precipitation of aragonite in cave environments, specific boundary conditions must be fulfilled. In detail, dripwater pH > 8.2, dripwater Mg/Ca > 0.5, and the calcite saturation index < 0.8 (Riechelmann et al., 2014). However, if dripwater pH < 8.2 or the calcite saturation index > 0.8, calcite will continue to precipitate even though dripwater Mg/Ca > 0.5 (see, for example, drip site BM8 in Bab Mafraque Cave (Riechelmann et al. 2014). Therefore, a change from calcite to aragonite within a speleothem does not always reflect a change in the trace element composition of the dripwater. In addition, calcite and aragonite can co-precipitate from dripwaters with only slightly different chemical composition. This result is corroborated by the existence of lateral Cc-Ar transitions in samples HK1 (Wassenburg et al., 2012), KRUM11 and MO. Therefore, the balance between all three dripwater characteristics (i.e., pH, calcite saturation index, and Mg/Ca) is delicate, and only a small, short-lived (i.e., seasonal - annual) change in one of these parameters can initiate precipitation of aragonite. Furthermore, it is energetically advantageous to continue precipitating the same mineral (termed “syntaxial overgrowth”, Fairchild and Baker, 2012). Thus, the return to the same precipitation conditions does not necessarily initiate calcite precipitation. In short, very minor water chemistry changes could surpass a threshold, triggering a sudden shift from calcite to aragonite. Large shifts in water chemistry are neither required nor necessarily implied.

3.6. Sample and trace element data selection

The samples and trace element/Ca ratios selected for the calculations are subject to strict criteria. Post-depositional diagenesis may alter the trace element composition of both aragonite (Lachniet et al., 2012; Ortega et al., 2005) and calcite speleothems (Scholz et al., 2014). Consequently, data derived from diagenetically altered sections were avoided. In addition, only pure calcite and aragonite phases were used. This is important because even a small amount of co-precipitated calcite (~2%) may have a large effect on the Mg/Ca ratio of aragonite (Wassenburg et al., 2012). Likewise, a small amount of co-precipitated aragonite may have a significant effect on the U/Ca ratio of calcite. Just before and after the change in speleothem mineralogy, co-precipitation of both calcite and aragonite is the rule rather than the exception. Usually, co-precipitation is spatially restricted and causes characteristic spikes in the trace element data. Therefore, the selection of the first datapoint closest to the Cc-Ar transition is based on the absence of spikes in the aragonite Mg/Ca data and the calcite U/Ca data, which are both indicators of co-precipitation. This selection process implies that lateral Cc-Ar transitions are not suitable for determination of distribution coefficients with this strategy because at such sites co-precipitation is very likely to occur. However, due to the slightly higher porosity associated with a larger surface area and higher number of sites for nucleation, it is reasonable to expect that co-precipitation occurs preferentially within aragonite zones. Therefore, the largest offsets are expected for $D_{Mg(Ar)}$, whereas the effect should be negligible for $D_{Sr(Ar)}$, $D_{Ba(Ar)}$ and $D_{U(Ar)}$ because calcite Sr, Ba and U concentrations are low compared to those in aragonite. Consequently, we use data from two lateral Cc-Ar transitions from stalagmite HK1 (Wassenburg et al., 2012) to verify the values obtained from stratigraphical Cc-Ar transitions in this study. Furthermore, a minimum of several years of trace element data was averaged in order to avoid a bias towards extreme years; at least seven data points are used to calculate the mean X/Ca values for the calcite and aragonite to increase the statistical robustness. This minimum number of points is related to the maximum number of laser spots available for the shortest speleothem section studied (stalagmite HBSH1).

4. Results and interpretation

4.1. Petrography and degree of preservation

Petrographic studies on the previously published samples indicate that the analysed calcite and aragonite fabrics represent primary mineralogies with only very subtle, if any, diagenetic features (McMillan et al., 2005; Wassenburg et al., 2012). The petrography and degree of preservation of the newly analysed samples is described in the paragraphs below.

388

389 4.1.1. Stalagmite MAW4

390 The calcite portion of stalagmite MAW4 (Fig. 3a-c) shows discontinuous, inclusion-
391 rich layers composed of non-ordered, relatively small (10-100 µm wide) calcite crystals
392 (Fig. 3b). In between these layers, columnar, radiaxial calcite crystals occur (Neuser and
393 Richter, 2007; Richter et al., 2011) (Fig. 3b). Directly beneath an aragonite interval, calcite
394 fabrics consisting of fan-like structures with a sweeping extinction over several crystals exist
395 (Figs. 3a and 4d).

396 The aragonite fabrics consist of needle-like crystals, elongated along their c-axis,
397 organized in fans with a sweeping extinction across several crystals (Fig. 3a). This specific
398 type of fabric has been referred to as acicular by Frisia and Borsato (2010). A series of thin
399 brown layers alternating with translucent white layers that are possibly seasonal in origin has
400 been observed, similar to sample MAW-0201 from the same cave (Myers et al., 2015).

401 The small, non-ordered calcite crystals may represent competitive growth occurring
402 after a growth interruption and are regarded as primary, similar to the columnar, radiaxial
403 calcite. However, the fan-like calcite has a very similar structure as the acicular aragonite.
404 This may represent the product of a fabric-preserving aragonite-to-calcite transformation
405 (Martin-Garcia et al., 2009; Perrin et al., 2014). Therefore, this specific calcite fabric was
406 avoided for the calculations, and only well-preserved columnar calcite fabrics were used.
407 Aragonite fabrics lack signs of micritization, dissolution and aragonite-to-calcite
408 transformation and are thus considered primary.

409

410 4.1.2. Stalagmite KRUM11

411 The calcite fabric of stalagmite KRUM11 appears as mosaic-like in thin sections
412 (Figs. 3d-f) (Frisia and Borsato, 2010), whereas the aragonite directly above the calcite shows
413 an acicular fabric (Frisia and Borsato, 2010) (Fig. 3e). Under plane polarized light, darker,
414 non-translucent zones alternate with translucent crystals within the aragonite (Fig. 3f).

415 A calcite mosaic fabric is usually interpreted as a result of diagenesis (Frisia and
416 Borsato, 2010; Scholz et al., 2014). However, the calcite did not show any aragonite relicts or
417 dissolution features, and the cross section shown in Figs. 3d-f is not parallel to the c-axis of
418 the crystals, therefore, this calcite was considered to be of primary nature. The aragonite of
419 KRUM11 shows some opaque, non-translucent layers, which appear as micritized aragonite
420 (Fig. 3f). Therefore, this Cc-Ar transition has been excluded for the calculations of the
421 speleothem aragonite distribution coefficients.

422

423 4.1.3. Stalagmite HBSH1

424 The calcite layers within stalagmite HBSH1 are 5-10 mm thick and consist of
425 columnar calcite crystals. The aragonite has an acicular fabric characterised by a sweeping
426 extinction pattern across several crystals (Fig. 3g). The individual crystals are somewhat
427 longer and wider compared to those from stalagmite MAW4 (Fig. 2), and individual needle-
428 like aragonite crystals and spherulites are distributed between the relatively long and wide
429 aragonite crystals (Fig. 3g). No diagnostic features of diagenesis (e.g., micritization,
430 dissolution or calcite-to-aragonite transformation) are apparent, and the fabrics are therefore
431 considered primary.

432

433 4.1.4. Flowstone MO

434 Flowstone MO consists of an elongated columnar, radiaxial calcite fabric with an
435 undulose extinction (Richter et al., 2011). The aragonite consists of clear, translucent crystals
436 belonging to an acicular fabric (Fig. 3i-j) (Frisia and Borsato, 2010). Both calcite and
437 aragonite do not show any sign of diagenetic alteration, and thus represent primary material.

438

439 4.2. Conditions of formation

440

441 4.2.1. Timing of calcite-to-aragonite transitions and determination of speleothem growth rates

442 Five samples from flowstone MO were dated. Four samples were beyond the dating
443 limit of the ^{230}Th/U-method. The top sample was dated at 106.9 ± 1.1 ka (Fig 2; Table 3).

444 The calcite phase of stalagmite KRUM11 occurred between 16.89 ± 0.11 and
445 16.42 ± 0.12 ka (Fig. 2; Table 3). The mean growth rate for this section is ca. 35 µm/a.

446 Sample MAW4 was actively growing at the time of collection (2006 AD). The
447 aragonite samples were dated at -0.0476 ± 0.0018 and -0.0202 ± 0.0013 ka (Fig. 2; Table 3),
448 revealing high growth rates with a mean of ~293 µm/a. The two calcite samples were dated at
449 0.202 ± 0.011 and 0.395 ± 0.055 ka (Fig. 2; Table 3), which corresponds to a much lower
450 mean growth rate of ca. 24 µm/a.

451 Eight aragonite sub-samples bracketing four Cc-Ar transitions in stalagmite HBSH-1
452 were dated (Table 3). The corresponding ages are between 216.6 ± 2.8 and 78.66 ± 0.81 ka
453 (Table 3). The corresponding growth rates for the four Cc-Ar transitions are between 1 and
454 11 µm/a. All growth rates are based on linear interpolation between two subsequent samples.

455

4.2.2. Temperature at time of deposition

Day and Henderson (2013) documented that calcite D_{Mg} and D_U in precipitation experiments depend on temperature. In particular, $D_{U(Cc)}$ is 0.11 at 7°C and 0.12 at 15°C, whereas $D_{Mg(Cc)} = 0.01*e^{0.02*T}$. Although the temperature dependency of $D_{Mg(Cc)}$ is relatively small in comparison to cave site temperature variations, an approximate assessment of cave temperatures is considered important here.

Cave temperature at the time of the Cc-Ar transitions in the investigated samples are estimated using modern cave temperature compiled in the context of cave monitoring programs (Table 1) (Breitenbach et al., 2015; Frisia et al., 2002; Riechelmann et al., 2014; Wassenburg et al., 2013), geographical location of the cave sites (Table 1), and the timing of the growth phases of the Cc-Ar transitions (Table 3). MAW4, KRUM11, HK3, GP2 and CL26 cave air temperatures must have been closer to 15 than to 7°C (Table 4). Thus, we use the higher calcite D_U of 0.12 (Day and Henderson, 2013). For flowstone MO, the timing of the Cc-Ar transition is unknown, and formation temperature is not quantifiable. However, we use the modern cave air temperature of 13°C for the calculations and, consequently, a D_U value of 0.12.

Three of the four Cc-Ar transitions from stalagmite HBSH1 grew within the time interval from 131 and 79 ka BP. For each of these transitions, we use a temperature estimate from a pollen and plant macrofossil record from central Germany (Kühl et al. (2007). This record suggests mean January temperatures of -12°C and mean July temperatures of 17.5°C, which corresponds to a mean annual temperature of ~3°C. For the oldest Cc-Ar transition in stalagmite HBSH1, which occurred around 216 ka BP (Marine Isotope Stage 7; Table 3), no temperature estimate can be derived due to a lack of data. Therefore, we assume the same temperature as for the other Cc-Ar transitions from stalagmite HBSH1 (Table 4). Consequently, a D_U value of 0.11 was used for all four mineralogical transitions found within stalagmite HBSH1.

4.3. Distribution coefficients

4.3.1. Trace element data

Trace element data across the Cc-Ar transitions from the different speleothems are presented in Fig. 5. The line scan data reproduce the single spot analyses very well indicating sample homogeneity at the sub-millimeter scale. The Cc-Ar transitions are clearly visible in Mg/Ca, Sr/Ca, Ba/Ca and U/Ca ratios (Fig. 5). As expected, Sr/Ca, Ba/Ca and U/Ca ratios are

higher in aragonite, whereas Mg/Ca is higher in calcite. For sample MAW4, a stepwise increase (decrease) in Sr/Ca and U/Ca (Mg/Ca) is apparent starting ca. 3 mm below the Cc-Ar transition and is followed by the actual Cc-Ar transition. A more detailed discussion is required to clarify which data are most useful for the calculations of the aragonite distribution coefficients.

Stalagmite MAW4 shows a fan-like calcite fabric (Fig. 3a-c), which is interpreted as the result of aragonite-to-calcite transformation. It is possible that the intermediate values of Sr/Ca, U/Ca and Mg/Ca are associated with this fabric because it is common that secondary calcite may preserve the trace element signature of the precursor aragonite (Niggemann and Richter, 2006). However, the thin section was taken from another portion of stalagmite MAW4, thus preventing establishing a direct link with the trace element data. Therefore, an area close to the trace element transect was mapped with Raman spectroscopy, which indicated that both phases with the intermediate (Cc1) and high (Cc2) Mg/Ca ratios are indeed calcite with negligible aragonite (Fig. 4). Sr/Ca and U/Ca ratios are higher, and the Mg/Ca ratios are lower in Cc1 than in Cc2, suggesting that aragonite-to-calcite diagenesis may have affected Cc1. Consequently, only the trace element data derived from Cc2 are used to calculate distribution coefficients.

4.3.2. Speleothem aragonite distribution coefficients

The trace element/Ca ratios used to calculate speleothem aragonite $D_{X(Ar)}$ are shown in Fig. 5 and Table 4. The time represented by each calcite or aragonite trace element value used for the calculation varies from sample to sample, ranging from 2 to 771 years (Table 4). We acknowledge that 771 years seems unreasonably long for the discussion of transitions. However, the corresponding sample (HBSH1-20) has a growth rate of only 1 µm/a, and it is necessary to calculate a mean X/Ca value based on multiple data points to obtain a reliable estimate of both the X/Ca value and its uncertainty for the calculations. For stalagmite MAW4, only the calcite part with the highest Mg/Ca ratios (Cc2) was used in order to prevent a bias due to diagenetically altered calcite (see above).

The calculated aragonite distribution coefficients with associated uncertainties are presented in Table 5 and Fig. 6. The mean aragonite $D_{Mg(Ar)}$ is $9.7*10^{-5} \pm 9.0*10^{-5}$, $D_{Sr(Ar)}$ is 1.38 ± 0.53, $D_{Ba(Ar)}$ is 0.91 ± 0.88, and $D_{U(Ar)}$ is 6.26 ± 4.53. $D_{X(Ar)}$ values calculated from stalagmite HBSH1 are higher for all elements examined and increase standard deviations significantly (Table 6). This is especially the case for $D_{Ba(Ar)}$, which changes from 0.91 ± 0.88 to 0.46 ± 0.18 if the values calculated from stalagmite HBSH1 are excluded (Table 6).

Despite the uncertainty, the results demonstrate for the first time that under karst environmental conditions $D_{Mg(Ar)}$ is considerably smaller than one, $D_{Sr(Ar)}$ is above one or close to unity, and $D_{U(Ar)}$ is larger than one. As noted earlier, we used the trace element datasets covering two lateral Cc-Ar transitions from stalagmite HK1 (Wassenburg et al., 2012) to verify the $D_{Sr(Ar)}$, $D_{Ba(Ar)}$ and $D_{U(Ar)}$ derived from stratigraphical Cc-Ar transitions. The corresponding $D_{X(Ar)}$ values are indistinguishable from those derived using stratigraphic Cc-Ar transitions adding confidence to the validity of our estimates (Fig. 6). The large difference in growth rate between the aragonite (295 µm/a) and the calcite (24 µm/a) sections of stalagmite MAW4 does not seem to affect the calculated aragonite $D_{X(Ar)}$ value because the results are consistent with the other values.

5. Discussion

To our knowledge, this is the first attempt to quantify speleothem aragonite $D_{X(Ar)}$ values (other than the determination of $D_{U(Ar)}$ of Jamieson et al. (submitted). Although our approach is relatively simple, the results are consistent for most transitions (in particular for aragonite D_{Sr}) (Fig. 6). This indicates that the incorporation mechanisms are similar for calcite and aragonite, which is a basic requirement for the application of the concept of a distribution coefficient (Fairchild and Treble, 2009). However, the values calculated using stalagmite HBSH1 are higher. Furthermore, the calculated $D_{Mg(Ar)}$, $D_{Ba(Ar)}$ and $D_{U(Ar)}$ values show large variability (Fig. 6). Variable environmental conditions and dripwater chemistry characteristics of the different samples may partially explain these differences. Environmental factors, such as temperature, drip rate, precipitation rate, and solution composition, may contribute to the large spread in both calcite and aragonite D_X values. However, we emphasize that the chemical composition of the dripwaters must have been similar across all transitions because aragonite only tends to precipitate in case of dripwater Mg/Ca ratios $\geq$0.6 and dripwater pH $\geq$8.2 and a relatively low ($\leq$0.8) saturation-index with respect to calcite (Riechelmann et al., 2014).

5.1. Sensitivity analysis

Although only the best available speleothem samples with calcite-aragonite transitions were used, the calculated aragonite $D_{X(Ar)}$ values of course depend on the data selected for the calculations. To assess any selection bias, all calculations were repeated with trace element data representing only 2-155 years of stalagmite growth instead of 2-771 years. This transect consisting of 2-155 years of data comprises the part of the original trace element transect of 2-

771 years closest to the Cc-Ar transition. This sensitivity analysis was performed on each sample (input parameters used for the corresponding calculations are given in supplemental Table EA1). The median $D_{X(Ar)}$ values of both datasets are comparable (Table 6), indicating that the calculated $D_{X(Ar)}$ values do not strongly depend on the selected trace element transect. Nevertheless, the mean X/Ca ratio calculated using the longer dataset should be statistically more robust, and is thus the preferred value.

In addition to varying the number of trace element data points, the results were tested using an aragonite-to-calcite transition from stalagmite HK3 (Wassenburg et al., 2012). We applied the same approach to the data from the Ar-Cc transition to calculate the calcite distribution coefficient by using the aragonite distribution coefficient. Using the same error propagation as for the calculated aragonite distribution coefficients, the calculated calcite distribution coefficients are 0.019 ± 0.004, 0.14 ± 0.02, 0.13 ± 0.02 and 0.13 ± 0.05 for $D_{Mg(Cc)}$, $D_{Sr(Cc)}$, $D_{Ba(Cc)}$ and $D_{U(Cc)}$, respectively. Although this transition was interpreted as a hiatus (Wassenburg et al. 2012), $D_{X(Cc)}$ values calculated across this transition are, with exception of $D_{Mg(Cc)}$, within error of the $D_{X(Cc)}$ values reported by Day and Henderson (2013). We refer to section 5.5 for a detailed discussion of D_{Mg}. These cross-validations provide further support that our approach yields reliable results.

5.2. Rayleigh distillation effects

Varying amounts of Rayleigh distillation occurring on stalagmite surfaces affect all trace element distribution coefficients in a similar way (Johnson et al., 2006). The amount of Rayleigh distillation controls the apparent D_X value and depends on (i) drip rate, which controls the mixing between the solution on top of the stalagmite and the impinging drop (Mühlinghaus et al., 2009), and (ii) super-saturation of the dripwater with respect to $CaCO_3$, which controls the precipitation rate. Different drip sites are therefore characterized by varying degrees of Rayleigh distillation and a range of apparent D_X values. The Rayleigh distillation effect depends on the amount of Ca^{2+} that precipitates during a single drip interval, i.e. the excess of Ca. Consequently, drip sites with similar $CaCO_3$ deposition rates are characterized by small excess Ca^{2+} if (i) drip intervals are short, because there is little time to precipitate $CaCO_3$ until replenishment of the water at the top of the stalagmite, (ii) dripwater Ca concentration is high, and (iii) the water film covering the stalagmite surface is thick (because it takes longer for dripwater to reach a higher supersaturation). Here we calculate mean $CaCO_3$ deposition rates using the ^{230}Th/U-based speleothem growth rates:

$$r = \frac{v*\sigma*9.48151*10^{-4}}{31536000}, \quad (6)$$

where r is the average $CaCO_3$ deposition rate (mmol/cm^2/s), v is the speleothem growth rate (µm/year), and σ is the density of aragonite (g/cm^3). With assumptions for drip rate, initial dripwater Ca^{2+} concentration and film thickness, the amount of Ca removed from the dripwater per drip can be calculated for every Cc-Ar transition using the equation from Stoll et al. (2012):

$$Ca - excess = \frac{r*\Delta t/\delta}{Ca_i}, \quad (7)$$

where δ is the thickness of the water film (cm), Δt is drip interval (s), and Ca_i is initial Ca concentration (mmol/cm^3). The boundary conditions were chosen relatively conservative, such that the calculated excess Ca^{2+} represents an overestimation rather than an underestimation. In particular, we assumed a very long drip-interval of 600 s (10 min), a low initial dripwater Ca concentration of 20 mg/l and a realistic film thickness of 0.01 cm (Baker et al., 2014; Hansen et al., 2013). The estimated amount of excess Ca^{2+} precipitation ranges from 0.08 to 3.9% (Table 5), except for stalagmite MAW4 aragonite, for which a value of 19% is estimated. With only 0.08 to 3.9% of excess Ca^{2+} precipitation during one drip interval, Rayleigh distillation effects are minimal and within the range of our analytical uncertainties. For MAW4, an influence of Rayleigh distillation on the calculated aragonite $D_{X(Ar)}$ values cannot be excluded. However, we emphasize that an initial dripwater Ca concentration of 20 mg/l for the dripwater is very low, and typical values range from 30 to 90 mg/l (Frisia et al., 2002; Karmann et al., 2007; Riechelmann et al., 2011; Tremaine and Froelich, 2013). Drip sites with lower dripwater Ca^{2+} concentrations are usually associated with low $CaCO_3$ saturation indices and low precipitation rates.

5.3. Speleothem aragonite $D_{Sr(Ar)}$

The aragonite $D_{Sr(Ar)}$ values calculated from the different calcite-to-aragonite transitions are in mutual agreement (Fig. 4), with the exceptions of values calculated from HBSH-1 (which are higher than the other values) and stalagmite CL26 (lower than the other values) (Table 4). A comparison with published aragonite $D_{Sr(Ar)}$ values shows that the mean value derived from all transitions is in a similar range as the values based on marine analogue laboratory experiments (Table 6).

625 The calculated aragonite $D_{Sr(Ar)}$ values depend on the value used for $D_{Sr(Cc)}$ of calcite.
626 Calcite $D_{Sr(Cc)}$ is known to be dependent on solution composition (Mucci and Morse, 1983;
627 Pingitore and Eastman, 1986), precipitation rate (Gabitov and Watson, 2006; Treble et al.,
628 2005), and possibly competition effects (Borsato et al., 2007). The latter may be related to the
629 availability of impurities in the crystal lattice, which in turn may be controlled by the
630 incorporation of Mg. The application of a universal $D_{Sr(Cc)}$ for all Cc-Ar transitions may
631 therefore not be appropriate.
632 Precipitation experiments from Mucci and Morse (1983) showed that the incorporation
633 of small sized Mg-ions is accompanied by increasing incorporation of larger Sr-ions. This
634 relationship appeared to be linear and is expressed by $D_{Sr(Cc)} = 0.146 + 0.01833 * \%MgCO_3$.
635 Although it is tempting to use this relationship to correct the calcite $D_{Sr(Cc)}$ values used for the
636 calculations, we do not consider this as a suitable approach since the precipitation
637 experiments from Mucci and Morse (1983) reflect marine conditions. In addition, a calcite
638 $D_{Sr(Cc)}$ value of 0.146 in absence of Mg seems high in comparison to the values reported from
639 cave precipitation experiments (Tremaine and Froelich, 2013). However, the laboratory
640 precipitation experiments of Day and Henderson (2013) were specifically designed to mimic
641 the solution composition of caves with a limestone host rock, and used dripwater Mg/Ca
642 ratios of 0.047. In our study, the calculated dripwater Mg/Ca ratios of all samples are between
643 0.6 and 2.8, reflecting the high Mg content of the corresponding host rock (Table 1).
644 Therefore, calcite $D_{Sr(Cc)}$ may have been generally underestimated resulting in an
645 underestimated value of aragonite $D_{Sr(Ar)}$. Since the calcite of HBSH1 is characterized by the
646 lowest Mg/Ca ratios, the aragonite $D_{Sr(Ar)}$ value calculated from HBSH1 may be least affected
647 by the underestimation of calcite $D_{Sr(Cc)}$.
648 Stalagmite CL26 provided aragonite D_{Sr} values <1 (0.70; Fig. 6, Table 5). Even
649 considering a calcite $D_{Sr(Cc)}$ value of 0.15 (McMillan et al., 2005) results in an aragonite
650 $D_{Sr(Ar)}$ value of 0.87. This value is still lower than the mean value calculated from the four Cc-
651 Ar transitions from stalagmite HBSH1 (1.83 ± 0.46). Considering the relatively similar
652 growth rates of 50 µm/a for stalagmite CL26 and 10 µm/a for HBSH1, a large growth rate
653 effect on calcite $D_{Sr(Cc)}$ is unlikely. Furthermore, Pingitore and Eastman (1986) showed that
654 calcite $D_{Sr(Cc)}$ increases with lower calcite Sr/Ca ratios. However, the calcite Sr/Ca ratios of
655 stalagmite HBSH1 are comparable to those of the other samples (Table 4). Thus, the different
656 values obtained from the different stalagmites may be realistic and explicable by differing
657 factors controlling aragonite $D_{Sr(Ar)}$.

Precipitation experiments suggest that aragonite $D_{Sr(Ar)}$ is higher at lower temperatures, and is defined by $D_{Sr(Ar)} = 1.27 - 0.005212*T$ (Dietzel et al., 2004). Stalagmite HBSH1 grew in central Europe during the Last Glacial with an estimated mean annual cave temperature of 3°C. All other samples grew under warmer conditions, i.e., between 12°C and 18°C (Table 4). However, according to the temperature expression from Dietzel et al. (2004), a temperature difference of 10°C would only result in a difference of 0.05 for $D_{Sr(Ar)}$, insufficient to explain the observed difference.

Gabitov et al. (2006) reported that Sr incorporation into aragonite shows little dependency on growth rate. However, their experiments were conducted at precipitation rates of 2-117 µm/day, which is not comparable to the slow growth rates of the speleothem samples examined here. Figure 7 suggests a growth rate dependency of aragonite $D_{Sr(Ar)}$, but only for (very) slow growth rates in the range of 1-20 µm/a. For higher growth rates, $D_{Sr(Ar)}$ seems to converge to values around 1.01 (±0.18), a value that overlaps with the results reported from marine analogue precipitation experiments (Table 6). We emphasize that calcite $D_{Sr(Cc)}$ has not been corrected with respect to its Mg/Ca ratio and that the relationship is only based on a small number of data points. In addition, uncertainties in the calculated speleothem growth rate related to dating uncertainties indicate that this suggestion should be considered with caution. Nonetheless, growth rate could be a potential factor, which may be important when interpreting Sr signals of slowly growing aragonite speleothems. Lower growth rates may be associated with higher aragonite $D_{Sr(Ar)}$, contrasting the relationship between growth rate and calcite $D_{Sr(Cc)}$.

5.4. Speleothem aragonite $D_{Ba(Ar)}$

Both Ba and Sr are characterized by large ionic radii and have similar chemical properties. Therefore, their partitioning into aragonite and calcite is similar. Indeed, precipitation experiments indicate that calcite $D_{Ba(Cc)}$ and calcite $D_{Sr(Cc)}$ are similar (Day and Henderson, 2013) and increase with increasing growth rates (Tesoriero and Pankow, 1996). Aragonite $D_{Ba(Ar)}$ and $D_{Sr(Ar)}$ respond in a similar manner to temperature changes, i.e., both Ba and Sr incorporation decrease with increasing temperature (Dietzel et al., 2004; Gaetani and Cohen, 2006). Similarly as for Sr, the relatively large ionic radius of Ba results in preferential incorporation into the aragonite crystal lattice, and aragonite $D_{Ba(Ar)}$ is (as $D_{Sr(Ar)}$) expected to be >1, at least for temperatures below 40°C (Dietzel et al., 2004; Gaetani and Cohen, 2006) (Table 6). However, only two of our aragonite $D_{Ba(Ar)}$ values calculated from Cc-Ar

transitions in stalagmite HBSH1 meet this expectation, all other values have a mean of 0.46 ±0.18 (Table 6; Fig. 6).

Values of aragonite $D_{Ba} < 1$ have been reported for temperatures of 40°C and higher (Dietzel et al., 2004; Gaetani and Cohen, 2006). Such temperatures are not expected for cave environments unless they are strongly affected by hydrothermal fluids. Furthermore, aragonite $D_{Ba(Ar)}$ seems to be independent of growth rate. As for Sr, solution composition (i.e., high Mg/Ca ratios) and an underestimation of calcite $D_{Ba(Cc)}$ may explain this potential underestimation of aragonite $D_{Ba(Ar)}$. The ionic radii of Ca, Sr and Ba in sixfold coordination are 1.08, 1.21 and 1.44 Å, respectively. Because Ba has the largest ionic radius, increased Mg incorporation may affect calcite $D_{Ba(Cc)}$ more strongly than calcite $D_{Sr(Cc)}$, although this idea has not been tested yet. Thus, it remains unclear whether this effect would be sufficient to explain the observed difference with published aragonite $D_{Ba(Ar)}$ values derived from precipitation experiments mimicking marine environments. It is possible that in cave environments, Ba incorporation into aragonite is prohibited through competition effects with other large cations. Alternatively, Ba may also be incorporated to a substantial extent through adsorption to colloidal or particulate matter. In summary, our results show that aragonite $D_{Ba(Ar)}$ values derived from precipitation experiments reflecting marine environments should be considered with caution when applied to cave environments. Additional work is needed to clarify the incorporation mechanisms in detail.

5.5. Speleothem aragonite $D_{Mg(Ar)}$

Our calculated aragonite $D_{Mg(Ar)}$ values agree with the values reported by Gabitov et al. (2008) and Zhong and Mucci (1989) (Table 6), but Gaetani and Cohen (2006) found higher values (Table 6). The discrepancy between Gaetani and Cohen (2006) and other estimates may reflect different experimental setups and analytical techniques (Gabitov et al., 2008). The variability of our calculated speleothem aragonite D_{Mg} values is relatively large (Fig. 6), which is most likely related to the incorporation mechanism of Mg into aragonite because its ionic radius in six-fold coordination is only 0.80 Å. Therefore, it is very unlikely to substitute for Ca within the aragonite crystal lattice. Gabitov et al. (2008) found a strong precipitation rate effect and explained it by the growth entrapment model (Watson, 1996, 2004). According to this model, Mg is incorporated in equilibrium with the solution below a precipitation rate of 0.09 µm/day (i.e., 33 µm/a) (Gabitov et al., 2008), leading to Mg concentrations close to zero ppm. However, the aragonite sections of stalagmite HBSH1 are characterized by growth rates lower than 17 µm/a and contain 8 ppm Mg. Some studies showed that part of the Mg in

aragonite speleothems is associated with Al, Si, and Th, which was interpreted as detrital material (Yang et al., 2015; Wassenburg et al., 2013).

5.6. Speleothem aragonite $D_{U(Ar)}$

Our calculated aragonite $D_{U(Ar)}$ values are in a similar range as the relatively high values reported by Meece and Benninger (1993) (Table 6). Furthermore, Jamieson et al. (submitted) also uses speleothem calcite-to-aragonite transitions to calculate $D_{U(Ar)}$ and report a value of 3.74 ± 1.13, confirming our values. In contrast, Gabitov et al. (2008) found significantly lower aragonite $D_{U(Ar)}$ values, whereas Kitano and Oomori (1971) reported intermediate values (Table 6). As discussed by Gabitov et al. (2008), U is mostly incorporated into $CaCO_3$ as $UO_2(CO_3)_3$ (Reeder et al., 2000), which is most abundant at solution pH-values between 7.5 and 8 (Djogic et al., 1986). For pH-values in this range, high aragonite $D_{U(Ar)}$ values can thus be expected. However, Meece and Benninger (1993) performed experiments with pH-values between 8 and 8.8, which consequently should result in relatively low $D_{U(Ar)}$ values. As a consequence, U-incorporation into aragonite must be governed by multiple factors.

The largest speleothem aragonite $D_{U(Ar)}$ values in our study were derived from stalagmite HBSH1 (Table 6). HBSH1 is the sample with the lowest growth rate, indicating a low supersaturation with respect to $CaCO_3$ and consequently a low dripwater pH. Compared to the other samples, we thus argue that the pH values of the dripwater associated with stalagmite HBSH1 must have been the lowest, although still high enough to precipitate aragonite (i.e., 8.2, Riechelmann et al., 2014). The relatively high $D_{U(Ar)}$ values calculated from stalagmite HBSH1 may thus, at least partly, be assigned to the relatively low pH values of the dripwater.

Our calculated speleothem aragonite $D_{U(Ar)}$ values show a large variability (Fig. 6), which, at least in part, must be assigned to variable calcite $D_{U(Cc)}$ values used for the calculations. In calcite, UO_2 is likely incorporated in several different configurations and is presumed to have a destabilizing effect (Reeder et al., 2000). Although Kelly et al. (2003) indicated that UO_2 can substitute for Ca within calcite, calcite discriminates more strongly against UO_2-incorporation compared to aragonite (Reeder et al., 2000). Therefore, we suggest that in calcite speleothems a larger percentage of the bulk U is adsorbed to colloidal phases, of which the incorporation depends on multiple factors (Hartland et al., 2014), which might lead to more variable calcite $D_{U(Cc)}$ values and thus relatively high variability in speleothem $D_{U(Ar)}$.

6. Conclusions

Aragonite speleothems may serve as excellent climate archives due to their amenability to ^{230}Th/U dating, provided that potential environmental proxies (i.e., stable isotopes, trace elements) contained within them can be well understood. This study represents a significant improvement towards quantifying and understanding trace element partitioning in speleothem aragonite, which is a prerequisite to assessing the extent to which prior aragonite precipitation (PAP) has affected speleothem aragonite trace element variability. Of special interest is whether $D_{X(Ar)}$ is above or below one because this determines whether enhanced PAP is associated with lower or higher speleothem trace element concentrations.

We derive mean speleothem aragonite values for $D_{Mg(Ar)}$, $D_{Sr(Ar)}$, $D_{Ba(Ar)}$, and $D_{U(Ar)}$ of $9.7*10^{-5} \pm 9.01*10^{-5}$, 1.38 ± 0.53, 0.91 ± 0.88, and 6.26 ± 4.54, respectively. All estimated values indicate that $D_{Mg(Ar)} << 1$ and $D_{U(Ar)} > 1$ (with the exception of one value), and $D_{Sr(Ar)} > 1$ or around unity. For $D_{Ba(Ar)}$, the majority of our samples suggest values < 1, although a few values are > 1. Our values show considerable variability, which may be due to variable precipitation rates (particularly important for $D_{Sr(Ar)}$ and $D_{Mg(Ar)}$), pH (important for $D_{U(Ar)}$), temperature (important for $D_{Sr(Ar)}$ and $D_{Ba(Ar)}$) and uncertainties in the calcite $D_{X(Cc)}$ used for the calculations. Furthermore, our data suggest that speleothem aragonite $D_{Sr(Ar)}$ may be affected by precipitation rate if the speleothem growth rate is below 20 µm/a. Lower precipitation rates seem associated with higher $D_{Sr(Ar)}$, although this should be confirmed by additional work.

Even though the calculated $D_{X(Ar)}$ are associated with considerable uncertainties, this study provides the foundation for interpreting trace element concentrations in speleothem aragonite in terms of climate change. In particular, dry climate conditions may lead to lower karst recharge and enhanced prior aragonite precipitation, which results in lower speleothem U but higher Mg concentrations if prior aragonite precipitation is indeed the dominating process (for example, Jamieson et al., submitted). If $D_{Sr(Ar)}$ is above one, then dry climate conditions may also lead to lower speleothem Sr concentrations, although this remains to be confirmed by additional research.

7. Acknowledgements

This work is funded by the DFG (WA3532/1-1) to J.A. Wassenburg and internal funding at the University of Mainz. D. Scholz also acknowledges funding of the DFG (SCHO 1274/9-1). J. Baldini acknowledges the funding of ERC grant 240167. Ian Fairchild is thanked for providing trace element data from stalagmite CL26, and associated uncertainties

of Ba and U data. S. Mischel and Y. Kocot are acknowledged for providing cave air CO_2 concentrations from Hüttenbläserschachthöhle. J. Fietzke and Angela Min are thanked for performing the chemistry and measurements of the U/Th ages of flowstone MO and stalagmite MAW4, respectively. Cecilia Cetti is thanked for earlier work on stalagmite MAW4, whereas C. Myers is thanked for fieldwork assistance and providing sample KRUM11. The Bochum thin section lab is acknowledged for making the thin sections of stalagmites MAW4 and KRUM11. B. Stoll, U. Weis and B. Schwager are gratefully acknowledged for their help with measurements and chemistry performed at the Max-Planck-Institute for Chemistry, while L. Zehnder (ETH Zürich) is thanked for support with XRD analyses.

804 References

805

806 Baker, A.J., Mattey, D.P., Baldini, J.U.L., 2014. Reconstructing modern stalagmite growth from cave
807 monitoring, local meteorology, and experimental measurements of dripwater films. Earth
808 Planet. Sci. Lett. 392, 239-249.
809 Borsato, A., Frisia, S., Fairchild, I.J., Somogyi, A., Susini, J., 2007. Trace element distribution in
810 annual stalagmite laminae mapped by micrometer-resolution X-ray fluorescence: Implications
811 for incorporation of environmentally significant species. Geochim. Cosmochim. Acta 71,
812 1494-1512.
813 Breitenbach, S.F.M., Lechleitner, F.A., Meyer, H., Diengdoh, G., Mattey, D., Marwan, N., 2015. Cave
814 ventilation and rainfall signals in dripwater in a monsoonal setting - a monitoring study from
815 NE India. Chem. Geol. 402, 111-124.
816 Cheng, H., Edwards, R.L., Hoff, J., Gallup, C.D., Richards, D.A., Asmerom, Y., 2000. The half-lives
817 of uranium-234 and thorium-230. Chem. Geol. 169, 17-33.
818 Cheng, H., Edwards, R.L., Shen, C.C., Polyak, V.J., Asmerom, Y., Woodhead, J., Hellstrom, J.,
819 Wang, Y.J., Kong, X.G., Spotl, C., Wang, X.F., Alexander, E.C., 2013. Improvements in Th-
820 230 dating, Th-230 and U-234 half-life values, and U-Th isotopic measurements by multi-
821 collector inductively coupled plasma mass spectrometry. Earth Planet. Sci. Lett. 371, 82-91.
822 Cosford, J., Qing, H.R., Eglington, B., Mattey, D., Yuan, D.X., Zhang, M.L., Cheng, H., 2008. East
823 Asian monsoon variability since the Mid-Holocene recorded in a high-resolution, absolute-
824 dated aragonite speleothem from eastern China. Earth Planet. Sci. Lett. 275, 296-307.
825 Day, C.C., Henderson, G.M., 2013. Controls on trace-element distribution in cave-analogue calcite.
826 Geochim. Cosmochim. Acta 120, 612-627.
827 Dietzel, M., Gussone, N., Eisenhauer, A., 2004. Co-precipitation of Sr^{2+} and Ba^{2+} with aragonite by
828 membrane diffusion of CO_2 between 10 and 50°C. Chem. Geol. 203, 139-151.
829 Djogic, R., Sipos, L., Branica, M., 1986. Characterization of uranium(VI) in seawater. Limnology and
830 Oceanography 31, 1122-1131.
831 Edwards, R.L., Chen, J.H., Wasserburg, G.J., 1987. U-238 U-234-Th-230-Th-232 Systematics and the
832 Precise Measurement of Time over the Past 500000 Years. Earth Planet. Sci. Lett. 81, 175-
833 192.
834 Fairchild, I.J., Baker, A., 2012. Speleothem Science from process to past environments. Wiley-
835 Blackwell.
836 Fairchild, I.J., Borsato, A., Tooth, A.F., Frisia, S., Hawkesworth, C.J., Huang, Y.M., McDermott, F.,
837 Spiro, B., 2000. Controls on trace element (Sr-Mg) compositions of carbonate cave waters:
838 implications for speleothem climatic records. Chem. Geol. 166, 255-269.
839 Fairchild, I.J., Treble, P.C., 2009. Trace elements in speleothems as recorders of environmental
840 change. Quaternary Science Reviews 28, 449-468.
841 Fairchild, I.J., Spötl, C., Frisia, S., Borsato, A., Susini, J., Wynn, P.M., Cauzid, J., EIMF, 2010.
842 Petrology and geochemistry of annually laminated stalagmites from an Alpine cave (Obir,
843 Austria): seasonal cave physiology. Geological Society, London, Special Publications 336,
844 295-321.
845 Fietzke, J., Liebetrau, V., Eisenhauer, A., Dullo, C., 2005. Determination of uranium isotope ratios by
846 multi-static MIC-ICP-MS: method and implementation for precise U- and Th-series isotope
847 measurements. J. Anal. At. Spectrom. 20, 395-401.
848 Finch, A.A., Shaw, P.A., Holmgren, K., Lee-Thorp, J., 2003. Corroborated rainfall records from
849 aragonitic stalagmites. Earth Planet. Sci. Lett. 215, 265-273.
850 Finch, A.A., Shaw, P.A., Weedon, G.P., Holmgren, K., 2001. Trace element variation in speleothem
851 aragonite: potential for palaeoenvironmental reconstruction. Earth Planet. Sci. Lett. 186, 255-
852 267.
853 Frisia, S., Borsato, A., 2010. Karst, in: Alonso-Zarza, A.M., Tanner, L.H. (Eds.), Carbonates in
854 continental settings - facies, environments and processes. Elsevier, pp. 269-318.
855 Frisia, S., Borsato, A., Fairchild, I.J., McDermott, F., Selmo, E.M., 2002. Aragonite-calcite
856 relationships in speleothems (Grotte de Clamouse, France): Environment, fabrics, and
857 carbonate geochemistry. Journal of Sedimentary Research 72, 687-699.

858 Gabitov, R.I., Cohen, A.L., Gaetani, G.A., Holcomb, M., Watson, E.B., 2006. Growth rate dependence
859 of Mg, Sr, and U incorporation into aragonite: Experimental constraints on the origin of vital
860 effects, Amercian Geophysical Union, Fall Meeting, San Fransisco.
861 Gabitov, R.I., Gaetani, G.A., Watson, E.B., Cohen, A.L., Ehrlich, H.L., 2008. Experimental
862 determination of growth rate effect on U^{6+} and Mg^{2+} distribution between aragonite and fluid
863 at elevated U^{6+} concentration. Geochim. Cosmochim. Acta 72, 4058-4068.
864 Gabitov, R.I., Sadekov, A., Leinweber, A., 2014. Crystal growth rate effect on Mg/Ca and Sr/Ca
865 distribution between calcite and fluid: An in situ approach. Chem. Geol. 367, 70-82.
866 Gabitov, R.I., Watson, E.B., 2006. Distribution of strontium between calcite and fluid. Geochem.
867 Geophys. Geosyst. 7, 12.
868 Gaetani, G.A., Cohen, A.L., 2006. Element distribution during precipitation of aragonite from
869 seawater: A framework for understanding paleoproxies. Geochim. Cosmochim. Acta 70,
870 4617-4634.
871 Gascoyne, M., 1983. Trace-element partition-coefficients in the calcite water-system and their
872 paleoclimatic significance in cave studies. J. Hydrol. 61, 213-222.
873 Griffiths, M.L., Drysdale, R.N., Gagan, M.K., Frisia, S., Zhao, J.X., Ayliffe, L.K., Hantoro, W.S.,
874 Hellstrom, J.C., Fischer, M.J., Feng, Y.X., Suwargadi, B.W., 2010. Evidence for Holocene
875 changes in Australian-Indonesian monsoon rainfall from stalagmite trace element and stable
876 isotope ratios. Earth Planet. Sci. Lett. 292, 27-38.
877 Hansen, M., Dreybrodt, W., Scholz, D., 2013. Chemical evolution of dissolved inorganic carbon
878 species flowing in thin water films and its implications for (rapid) degassing of CO_2 during
879 speleothem growth. Geochim. Cosmochim. Acta 107, 242-251.
880 Hartland, A., Fairchild, I.J., Muller, W., Dominguez-Villar, D., 2014. Preservation of NOM-metal
881 complexes in a modern hyperalkaline stalagmite: Implications for speleothem trace element
882 geochemistry. Geochim. Cosmochim. Acta 128, 29-43.
883 Hill, C., Forti, P., 1997. Cave minerals of the world, 2nd ed. National Speleological Society, USA.
884 Hoffmann, D.L., Prytulak, J., Richards, D.A., Elliott, T., Coath, C.D., Smart, P.L., Scholz, D., 2007.
885 Procedures for accurate U and Th isotope measurements by high precision MC-ICPMS. Int. J.
886 Mass Spectrom. 264, 97-109.
887 Huang, H.M., Fairchild, I.J., Borsato, A., Frisia, S., Cassidy, N.J., McDermott, F., Hawkesworth, C.J.,
888 2001. Seasonal variations in Sr, Mg and P in modern speleothems (Grotta di Ernesto, Italy).
889 Chem. Geol. 175, 429-448.
890 Huang, Y.M., Fairchild, I.J., 2001. Distribution of Sr^{2+} and Mg^{2+} into calcite under karst-analogue
891 experimental conditions. Geochim. Cosmochim. Acta 65, 47-62.
892 Jochum, K.P., Scholz, D., Stoll, B., Weis, U., Wilson, S.A., Yang, Q., Schwalb, A., Börner, N., Jacob,
893 D.E., Andreae, M.O., 2012. Accurate trace element analysis of speleothems and biogenic
894 calcium carbonates by LA-ICP-MS. Chem. Geol. 318, 31-44.
895 Jochum, K.P., Stoll, B., Friedrich, M., Amini, M., Becker, S., Dücking, M., Ebel, D.S., Enzweiler, J.,
896 Hu, M., Kuzmin, D., Mertz-Kraus, R., Müller, W.E.G., Regnery, J., Sobolev, A., Wang, X.,
897 Zhan, X., 2009. Laser ablation-inductively couped plasma-mass spectrometry and its
898 application in geochemsitry, cosmochemistry and environmental research. Rock and mineral
899 analysis 28, 53-68.
900 Johnson, K.R., Hu, C.Y., Belshaw, N.S., Henderson, G.M., 2006. Seasonal trace-element and stable-
901 isotope variations in a Chinese speleothem: The potential for high-resolution paleomonsoon
902 reconstruction. Earth Planet. Sci. Lett. 244, 394-407.
903 Karmann, I., Cruz, F.W., Viana, O., Burns, S.J., 2007. Climate influence on geochemistry parameters
904 of waters from Santana-Perolas cave system, Brazil. Chem. Geol. 244, 232-247.
905 Kelly, S.D., Newville, M.G., Cheng, L., Kemner, K.M., Sutton, S.R., Fenter, P., Sturchio, N.C., Spotl,
906 C., 2003. Uranyl incorporation in natural calcite. Environmental Science & Technology 37,
907 1284-1287.
908 Kitano, Y., Oomori, T., 1971. The coprecipitation of Uranium with Calcium Carbonate. Journal of the
909 Oceanographical Society of Japan 27, 34-42.
910 Kühl, N., Litt, T., Scholzel, C., Hense, A., 2007. Eemian and Early Weichselian temperature and
911 precipitation variability in northern Germany. Quaternary Science Reviews 26, 3311-3317.
912 Lachniet, M.S., Bernal, J.P., Asmerom, Y., Polyak, V., 2012. Uranium loss and aragonite calcite age
913 discordance in a calcitized aragonite stalagmite. Quat. Geochronol., 1-12.

914 Lorens, R.B., 1981. Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite
915 precipitation rate. Geochim. Cosmochim. Acta 45, 553-561.
916 Martin-Garcia, R., Alonso-Zarza, A.M., Martin-Perez, A., 2009. Loss of primary texture and
917 geochemical signatures in speleothems due to diagenesis: Evidences from Castanar cave,
918 Spain. Sediment. Geol. 221, 141-149.
919 Mattey, D., Lowry, D., Duffet, J., Fisher, R., Hodge, E., Frisia, S., 2008. A 53 year seasonally resolved
920 oxygen and carbon isotope record from a modem Gibraltar speleothem: Reconstructed
921 dripwater and relationship to local precipitation. Earth Planet. Sci. Lett. 269, 80-95.
922 McDermott, F., 2004. Palaeo-climate reconstruction from stable isotope variations in speleothems: a
923 review. Quaternary Science Reviews 23, 901-918.
924 McMillan, E.A., Fairchild, I.J., Frisia, S., Borsato, A., McDermott, F., 2005. Annual trace element
925 cycles in calcite-aragonite speleothems: evidence of drought in the western Mediterranean
926 1200-1100 yr BP. J. Quat. Sci. 20, 423-433.
927 Meece, D.E., Benninger, L.K., 1993. The Coprecipitation of Pu and Other Radionuclides with Caco3.
928 Geochim. Cosmochim. Acta 57, 1447-1458.
929 Mucci, A., Morse, J.W., 1983. The Incorporation of Mg^{2+} and Sr^{2+} into Calcite Overgrowths -
930 Influences of Growth-Rate and Solution Composition. Geochim. Cosmochim. Acta 47, 217-
931 233.
932 Mühlinghaus, C., Scholz, D., Mangini, A., 2009. Modelling fractionation of stable isotopes in
933 stalagmites. Geochim. Cosmochim. Acta 71, 2780-2790.
934 Myers, C.G., Oster, J.L., Sharp, W.D., Bennartz, R., Kelley, N.P., Covey, A.K., Breitenbach, S.F.M.,
935 2015. Northeast Indian stalagmite records Pacific decadal climate change: Implications for
936 moisture transport and drought in India. Geophys. Res. Lett. 42.
937 Neuser, R.D., Richter, D.K., 2007. Non-marine radiaxial fibrous calcites - examples of speleothems
938 proved by electron backscatter diffraction. Sediment. Geol. 194, 149-154.
939 Niggemann, S., Richter, D.K., 2006. Ein mittelpleistozäner Aragonitstalagmit aus der B7-Höhle (NW-
940 Sauerland, Nordrhein-Westfalen). Die Höhle 57, 47-56.
941 Obert, J. C., Scholz, D., Felis, T., Brocas, W. M., Jochum, K. P., and Andreae, M. O., 2016. 230Th/U
942 dating of Last Interglacial brain corals from Bonaire (southern Caribbean) using bulk and
943 theca wall material. Geochimica et Cosmochimica Acta 178, 20-40.
944 Oomori, T., Kaneshima, H., Maezato, Y., Kitano, Y., 1987. Distribution coefficient of Mg^{2+} ions
945 between calcite and solution at 10-50°C. Marine Chemistry 20, 327-336.
946 Ortega, R., Maire, R., Deves, G., Quinif, Y., 2005. High-resolution mapping of uranium and other
947 trace elements in recrystallized aragonite-calcite speleothems from caves in the Pyrenees
948 (France): Implication for U-series dating. Earth Planet. Sci. Lett. 237, 911-923.
949 Peel, M.C., Finlayson, B.L., McMahon, T.A., 2007. Updated world map of the K¨oppen-Geiger
950 climate classification. Hydrol. Earth Syst. Sci. 11, 1633-1644.
951 Perrin, C., Prestimonaco, L., Servelle, G., Tilhac, R., Maury, M., Cabrol, P., 2014. Aragonite-Calcite
952 Speleothems: Identifying Original and Diagenetic Features. Journal of Sedimentary Research
953 84, 245-269.
954 Pingitore, N.E., Eastman, M.P., 1986. The Coprecipitation of Sr-2+ with Calcite at 25-Degrees-C and
955 1-Atm. Geochim. Cosmochim. Acta 50, 2195-2203.
956 Reeder, R.J., Nugent, M., Lamble, G.M., Tait, C.D., Morris, D.E., 2000. Uranyl incorporation into
957 calcite and aragonite: XAFS and luminescence studies. Environmental Science & Technology
958 34, 638-644.
959 Richter, D.K., Götte, T., Niggemann, S., Wurth, G., 2002. Cathodoluminescence of carbonate
960 speleothems: state of the art, in: Carrasco, F., Durán, J.J., Andreo, Y. (Eds.), Karst and
961 Environment, pp. 381-387.
962 Richter, D.K., Neuser, R.D., Schreuer, J., Gies, H., Immenhauser, A., 2011. Radiaxial-fibrous calcites:
963 A new look at an old problem. Sediment. Geol. 239, 23-36.
964 Ridley, H., Asmerom, Y., Baldini, J.U.L., Breitenbach, S.F.M., Aquino, V.V., Prufer, K.M., Culleton, B.J.,
965 Polyak, V.J., Lechleitner, F.A., Kennett, D.J., Zhang, M., Marwan, N., Macpherson, C.G., Baldini,
966 L.M., Xiao, T., Awe, J., Haug, G.H. (2015) Aerosol forcing of the position of the intertropical
967 convergence zone since AD 1550. Nature Geoscience 8, 195-200.

Riechelmann, D.F.C., Schroder-Ritzrau, A., Scholz, D., Fohlmeister, J., Spotl, C., Richter, D.K., Mangini, A., 2011. Monitoring Bunker Cave (NW Germany): A prerequisite to interpret geochemical proxy data of speleothems from this site. J. Hydrol. 409, 682-695.

Riechelmann, S., Schröder-Ritzrau, A., Wassenburg, J.A., Schreuer, J., Richter, D.K., Riechelmann, D.F.C., Terente, M., Constantin, S., Mangini, A., Immenhauser, A., 2014. Physicochemical characteristics of dripwaters: Influence on mineralogy and crystal morphology of recent cave carbonate precipitates. Geochim. Cosmochim. Acta 145, 13-29.

Scholz, D., Hoffmann, D.L., 2008. ^{230}Th/U-dating of fossil reef corals and speleothems. Quaternary Science Journal (Eiszeitalter und Gegenwart) 57, 52-77.

Scholz, D., Tolzmann, J., Hoffmann, D.L., Jochum, K.P., Spötl, C., Riechelmann, D.F.C., 2014. Diagenesis of speleothems and its effect on the accuracy of ^{230}Th/U-ages. Chem. Geol. 387, 74-86.

Sherwin, C., M., Baldini, J.U.L., 2011. Cave air and hydrological controls on prior calcite precipitation and stalagmite growth rates: implications for palaeoclimate reconstructions using speleothems. Geochim. Cosmochim. Acta 75, 3915-3929.

Stoll, H.M., Muller, W., Prieto, M., 2012. I-STAL, a model for interpretation of Mg/Ca, Sr/Ca and Ba/Ca variations in speleothems and its forward and inverse application on seasonal to millennial scales. Geochem. Geophys. Geosyst. 13, 27.

Swart, P.K., 2015. The geochemistry of carbonate diagenesis: The past, present and future. Sedimentology 62, 1233-1304.

Tan, L.C., Shen, C.C., Cai, Y.J., Lo, L., Cheng, H., An, Z.S., 2014. Trace-element variations in an annually layered stalagmite as recorders of climatic changes and anthropogenic pollution in Central China. Quaternary Res 81, 181-188.

Tesoriero, A.J., Pankow, J.F., 1996. Solid solution distribution of Sr^{2+}, Ba^{2+}, and Cd^{2+} to calcite. Geochim. Cosmochim. Acta 60, 1053-1063.

Treble, P.C., Chappell, J., Shelley, J.M.G., 2005. Complex speleothem growth processes revealed by trace element mapping and scanning electron microscopy of annual layers. Geochim. Cosmochim. Acta 69, 4855-4863.

Tremaine, D.M., Froelich, P.N., 2013. Speleothem trace element signatures: A hydrologic geochemical study of modern cave dripwaters and farmed calcite. Geochim. Cosmochim. Acta 121, 522-545.

Wassenburg, J.A., Immenhauser, A., Richter, D.K., Jochum, K.P., Fietzke, J., Deininger, M., Goos, M., Scholz, D., Sabaoui, A., 2012. Climate and cave control on Pleistocene/Holocene calcite-to-aragonite transitions in speleothems from Morocco: elemental and isotopic evidence. Geochim. Cosmochim. Acta 92, 23-47.

Wassenburg, J.A., Immenhauser, A., Richter, D.K., Niedermayr, A., Riechelmann, S., Fietzke, J., Scholz, D., Jochum, K.P., Fohlmeister, J., Schröder-Ritzrau, A., Sabaoui, A., Riechelmann, D.F.C., Schneider, L., Esper, J., 2013. Moroccan speleothem and tree ring records suggest a variable positive state of the North Atlantic Oscillation during the Medieval Warm Period. Earth Planet. Sci. Lett. 375, 291-302.

Watson, E.B., 1996. Surface enrichment and trace-element uptake during crystal growth. Geochim. Cosmochim. Acta 60, 5013-5020.

Watson, E.B., 2004. A conceptual model for near-surface kinetic controls on the trace-element and stable isotope composition of abiogenic calcite crystals. Geochim. Cosmochim. Acta 68, 1473-1488.

Wong, C.I., Banner, J.L., Musgrove, M., 2011. Seasonal dripwater Mg/Ca and Sr/Ca variations driven by cave ventilation: Implications for and modeling of speleothem paleoclimate records. Geochim. Cosmochim. Acta 75, 3514-3529.

Yang, Q., Scholz, D., Jochum, K.P., Hoffmann, D.L., Stoll, B., Weis, U., Schwager, B., Andreae, M.O., 2015. Lead isotope variability in speleothems - a promising new proxy for hydrological change? First results from a stalagmite from western Germany. Chem. Geol. 396, 143-151.

Zhang, H., Cai, Y., Tan, L., Qin, S., An, Z., 2014. Stable isotope composition alteration produced by the aragonite-to-calcite transformation in speleothems and implications for paleoclimate reconstructions. Sediment. Geol. 309, 1-14.

Zhong, S., Mucci, A., 1989. Calcite and aragonite precipitation from seawater solutions of various salinities: Precipitation rates and overgrowth compositions. Chem. Geol. 78, 283-299.

Figure captions

Figure 1. Sampling locations of the speleothems used in this study. 1) Grotte Prison de Chien, north-west Middle Atlas, Morocco. 2) Grotte de Piste, north-west Middle Atlas, Morocco. 3) Unnamed cave 8 km south of Treveles, Alpujaras, southern Spain. 4) Grotte de Clamouse, southern France. 5) Hüttenbläserschachthöhle, central Germany. 6) Krem Mawmluh Cave, Meghalaya plateau, north-east India. 7) Krem Umsynrang Cave, Meghalaya plateau, north-east India.

Figure 2. Slabs showing Cc-Ar transitions with the corresponding trace element transects and the positions of ^{230}Th/U-sampling. Blue dashed lines indicate boundaries between calcite and aragonite. Yellow and black arrows indicate speleothem growth direction. a-c) Stalagmite KRUM11. d-e) Stalagmite MAW4. f-g) Flowstone MO. h-i) Stalagmite HBSH1 part 4.

Figure 3. Thin section petrography of calcite and aragonite fabrics. a) Stalagmite MAW4, transition from undulose columnar calcite to calcite fans with sweeping extinction to acicular aragonite. The two calcite fabrics are separated by detrital material (cross-polarised light). b) Stalagmite MAW4, columnar undulose calcite (cross-polarised light). c) Stalagmite MAW4, undulose columnar calcite interbedded by two detrital layers. d) Stalagmite KRUM11, calcite (cross-polarised light). e) Stalagmite KRUM11, Cc-Ar transition with acicular aragonite. (cross-polarised light). f) Same as (e), but with plain polarized light. Arrows indicate primary aragonite (Ar-p) and potentially micritized aragonite (Ar-m). g) Stalagmite HBSH1, part 4, columnar calcite crystals and acicular aragonite (cross-polarised light). h) Same as (g), but with plain polarized light. i) Flowstone MO, undulose columnar calcite crystals and acicular aragonite (cross-polarised light). j) Same as (i), but with plain polarized light.

Figure 4. Results of Raman spectroscopy of stalagmite MAW4. Blue dashed lines indicate the main transition from calcite to aragonite. a) Scan from MAW4 with positions of linescan and spots indicated (red); Cc1 and Cc2 (separated by yellow dashed line) are also indicated. b) 5 µm resolution Raman spectroscopy map covering the aragonite, Cc1 and Cc2. The image is stretched in horizontal direction. c) 2 µm resolution Raman spectroscopy map covering Cc1 with very limited aragonite. Dark red represents aragonite, green represents calcite. d) Thin section of stalagmite MAW4 with Cc-Ar transition (cross-polarised light). e) 2 µm resolution

Raman spectroscopy map covering fan-like calcite and aragonite. Blue represents aragonite, pink represents calcite.

Figure 5. Molar trace element Mg/Ca, U/Ca, Sr/Ca and Ba/Ca ratios across the investigated Cc-Ar transitions. a) Flowstone MO, b) Stalagmite MAW4. c) Stalagmite HBSH1 part 4. Linescan (grey) and single spot (black) analyses, respectively, are indicated. For stalagmite HBHS1, only spot analyses are available. Linescan data are shown as 5-point running medians. Data marked by the red shaded bar represent the data from the calcite section that have been used for the calculations. Data marked by the brown shaded bar represents the data from the aragonite section that have been used for the calculations.

Figure 6. Compilation of the speleothem aragonite distribution coefficients calculated from the Cc-Ar transitions studied. Diamonds (squares) indicate values derived from stratigraphic (lateral) Cc-Ar transitions. Shaded error bars include an additional uncertainty of 50% on the trace element to Ca ratio of the dripwater. Note that the y-axis has a logarithmic scale. For reference, the black horizontal line indicates a distribution coefficient value of 1 for the elements Sr, Ba, and U.

Figure 7. Relation between speleothem aragonite D_{Sr} and growth rate. Linear regression for the five data points corresponding to growth rates < 20 µm/year and associated correlation coefficient and p-value is shown.